Conceiving Process Synthesis Methods for Biorefineries

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Abstract

Developments in chemical engineering, particularly in the area of process synthesis have been dominated by phenomena in petrochemical industries. This study demonstrated that the special characteristics of biomass, different from petroleum would lead to new approaches in biorefinery synthesis. Four key challenges were identified, namely raw material(s) selection, products selection, process integration and equipment selection, of which the first three were addressed. Several metrics for measuring mass and energy values were suggested for comparison of different potential raw material(s) and products quantitatively. In addition, material and material & process mapping were introduced to summarise raw material, product and process alternatives. The Evolutionary Optimisation method was also proposed in order to find biorefinery configuration. It included superstructure generation by considering predicted heuristics.

Modifications of the corn to ethanol dry-grind process were used to demonstrate the proposed method and tools. The predicted heuristic specified *separating high value components (oil and fibres) before they are converted into lower value derivatives (Distiller's Dried Grains and Solubles)*. The suggestions based on the proposed metrics were in accordance with those based on simulation results.

1. Introduction

Petrochemical industries have been the major producers of industrial products worldwide, including fuels, chemicals, materials and energy. Consequently, the development of chemical engineering, particularly in the area of process synthesis, has been dominated by phenomena in these industries. Current process synthesis methods are expected to be applicable in biorefinery synthesis; however, additional principles are required to address the special characteristic of biomass and its processes.

This paper briefly reviews the established process synthesis methods and the existing biorefinery concept, analysing the main differences between biorefineries and oil refineries. Four key challenges in biorefinery synthesis are identified, from which proposed process synthesis method and tools for biorefineries are developed. A case study involving modifications of the corn to ethanol dry-grind process is used to demonstrate their uses [for details see Pertiwi, 2009].

2. Theory
2.1 Process Synthesis

Process synthesis is a part of an innovation process that includes stages from the "need identification" to "plant operation and maintenance" [Siirola, 1996]. Areas of special interest for process synthesis are the basic chemistry, detailed chemistry, task identification, unit operations and basic plant engineering. Systematic approaches to process synthesis provide guidance for assessing the feasibility and flexibility of a process as a whole and will generate several alternatives corresponding to different design decisions before any detailed design [Dimian and Bildea, 2008]. These methods can also eliminate poor projects and poor process alternatives with a minimum of

effort [Douglas, 1988]. Moreover, they have been proven to reduce energy requirements by 50% and costs by 35% for chemical industries [Dimian and Bildea, 2008; Siirola, 1996].

So far there have been three approaches for producing feasible process representations [Siirola, 1996]: (a) Systematic Generation, (b) Evolutionary Modification and (c) Superstructure Optimisation. This classification is based on the initial state prior to the process synthesis activities. The first approach (a) develops process representations starting from scratch; the second (b), which is the most practicable, modifies existing processes, and the last approach (c) involves finding the best alternative from synthesis trees including many options. The first and second approaches use heuristics and algorithmic methods for optimization of the process; whereas the last uses mathematical programming.

Siirola & Rudd [1971] were among the earliest to use systematic process generation approaches. Their interactive computer program, Adaptive Initial Design Synthesizer (AIDES), consists of six major steps: reaction path, species allocation, task identification, task integration, utilities system and equipment design. Douglas [1985] formalised similar steps, emphasising the distinction of batch and continuous processes and dividing the separation processes into vapour and liquid separations.

The concept of Evolutionary Modification as a method for developing a new process follows three main steps: (1) generation of initial processes, (2) identification of evolutionary rules and (3) determination of the evolutionary strategy [Rousseau, 1987]. Generation of initial processes is possible by following heuristics, or by examining similar processes found in practice or in the literature. Heuristics can be generated by following the PAR (Predict, Authenticate/analyse, and Re-evaluate/Rethink) procedure, as follows [Turton et al., 2003].

1) **Predict -** This step is the precondition of the procedure. It represents the 'best prediction' of the solution and often involves making assumptions and applying heuristics based on experience. Calculations should be limited to using short-cut techniques or 'back-of-the-envelope'.

2) **Authenticate/Analyse –** This step involves doing research relative to the problem, seeking out relevant equations, relationships or, if possible, actual operational data and performing calculations leading toward 'the best possible solution'.

3) **Re-evaluate/Rethink -** This compares the prediction in the first step and the solution in the second step. Some revisions, removals or replacements to the assumptions of first step might be required, and the new assumptions can create a new heuristic.

Superstructure Optimisation is a structural optimisation, which usually involves both continuous and discrete integer variables (mixed-integer programming) and either linear or non-linear equations. Due to its complexity, such optimisation is considered to be impractical for all but simple processes [Seider, 2004]. The objective function for process optimisation is usually the profitability measures (e.g. Return on Investment (ROI), profit, payback period (PP), Internal Rate of Return (IRR)). General Algebraic Modelling System (GAMS) with its solvers (e.g. GAMS-XA solver; CONOPT3 for non-linear programming; CPLEX for mixed integer programming) has been used for structural optimisation. For linear and non-linear mixed-integer programming problems, most solvers use a branch and bound approach which guarantees an optimal solution if it is linear or convex non-linear [Edgar et al., 2001].

2.2 The Biorefinery Concept

There are various definitions for biorefinery in the literature [Burel, 2007; De Jong et al., 2006; NREL, 2008; Thran et al., 2008]. However, most of these do not consider the inclusion of food and feed in the spectrum of biorefinery products. The most comprehensive definition of biorefinery is provided by the International Energy Agency (IEA), Bioenergy Task 42, from which the definition is 'the sustainable processing of biomass into a spectrum of marketable products and energy'. This definition includes the following key words [Van Ree & Annevelink, 2007]:

- biorefinery: concepts, facilities, processes, cluster of industries,
- sustainable: maximising economics, minimising environmental aspects, fossil fuel replacement, socio-economic aspects are taken into account,
- processing: upstream processing, transformation, fractionation, thermo-chemical and/or biochemical conversion, extraction, separation, downstream processing,
- biomass: crops, organic residues, agro-residues, forest residues, wood, aquatic biomass,
- spectrum: more than one,

- marketable: a market (acceptable volumes & prices) already exists or is expected to become available in the near future,
- products: both intermediates and final products, i.e. food, feed, chemicals, and materials, and
- energy: fuels, power, heat.

This definition clearly includes the characteristic of process inputs and outputs, the type of processes involved and the performance of the whole process (including food and feed amongst the products). It also includes process conversions in addition to refining and purification. The whole process should be sustainable, i.e. considering economic, social and environmental aspects, which is achievable by producing more than one material and/or energy. These process aspects can be compared to those of oil refineries, as shown in Table 1.

3. Results and Discussion
3.1 Identification of Key Challenges in Biorefinery Synthesis

Four key challenges (described below) have been identified in association with the steps of AIDES of Siirola and Rudd [1971], namely raw material(s) selection, products selection, process integration and equipment selection. Several tools analogous to the work of Speight [2002] and Tong & Cannell [1983] were developed to address the first three challenges. The correlations between the four challenges and the respective tools are presented in Figure 1.

(A) Raw Material(s) Selection - For raw material selection, characterisation of the target biomass is necessary. *Grouping and lumping methods can be used for simplification*. This study suggests several possible metrics for raw material selection, two of which are Carbon Value and Energy Value. These metrics are analogous to the Chemical and Fuel Values suggested by Tong & Cannell [1983]. Carbon Value is the price of raw material per carbon mass unit while Energy Value is the price per energy unit. There could also be other metrics, such as Starch Value, Oil Value, Protein Value, Lignin Value or Cellulose Value, and biorefineries can be classified according to these components. In addition to the metrics mentioned, *biomass availability is also a useful factor in products selection decisions*. Figure 2 describes the proposed material mapping containing information on energy content and the main component of various biomass as well as tentative classifications of various biomass and the respective biorefineries.

By making an analogy with a feed-forward process control system, a biorefinery can be represented as a block diagram with biomass as the input, and all the different products as outputs. There can be variations in the purity of the materials due to the varied and complex nature of the biomass components. If the impurities do not affect the performance of the main process, no pre-treatment needs to be carried out. Once the main process and products are specified, the feedstock(s) properties should be modified to meet the required input of the process. *Special treatments can be implemented to diminish the effect of the impurity, either removing it or adding a particular substance to improve the quality of the system. Other potential products might be unavoidably produced during the process. Various feedstocks with the same main component should be equally suitable for a biorefinery, as long as existing impurities are minimised.*

(B) Products Selection - For product selection, there are approaches involving reaction route synthesis, i.e. finding some chemically possible product derivatives, by investigating similar products, or by separating the feedstock into its components. For example, carbon, hydrogen and oxygen as well as derivatives such as starch can be extracted from oxygenated-hydrocarbon compounds. In a similar way, sugars can be produced from ligno-cellulosics and amino acids from proteins.

Material & process mapping, inspired by the mapping of petrochemicals proposed by Speight [2002], is described in Figure 3. It contains information on potential processes and products for each main component/derivative of biomass. Some technology platforms from existing biorefinery concepts and technology roadmaps were used as starting points. Attention should be given to the segments of torrefied biomass and vitamins which are different from those of the material mapping in Figure 2. Biomass torrefaction is a thermochemical process applied to biomass in order to make its properties similar to those of coal [Bergman and Kiel, 2005]. Torrefied biomass is located in the same level of components because it is expected to be converted into syngas, which is one of the main platforms in biorefineries, besides sugars. Syngas is a mixture of carbon monoxide and hydrogen; therefore, it should be produced from materials containing carbon, hydrogen and oxygen. Certain operations might also produce some components, which are not worth recovering as chemicals or

materials. These could be disposed of as wastes or processed into fuel or energy, if feasible (See Figure 1).

Biorefineries should produce more than one marketable product and there should also be significant profit generated by the process. Product alternatives need to be screened and ordered according to the potential profits. *The suggested metrics for comparison are Chemical Value and Fuel Value* [Tong & Cannel 1983]. Chemical Value is the price of product per mass unit, while Fuel Value is the respective Chemical Value per energy unit.

Table 1: A Comparison of Process Aspects for Biorefineries and Oil Refineries

No	Item	Biorefineries	Oil Refineries
1	Feedstock	'Organic materials of recent biological origin' [Brown, 2003].	Petroleum
2	Building blocks	Building blocks for chemicals: 1,4 diacids (succinic, fumaric and malic), 2,5 furan dicarboxylic acid, 3 hydroxy propionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol, and xylitol/arabinitol [Werpy et al., 2004]	Ethylene, propylene, the C4 olefins (butadiene and butenes), benzene, toluene, xylenes (ortho, meta, and para) and methane [AIChE, 1993]
3	Main components	Sugars, starches, ligno-cellulose, oils/fats or proteins, water, vitamins and minerals	Hydrocarbons, sulphur, nitrogen, oxygen, metals, and other elements [Speight 2002].
4	Material properties - Composition - Variety - Availability - Durability - Stability - Form	- complex mixture - high variety - seasonal (renewable) - easily damaged - biodegradable - high solids content	- better known mixtures - less variety - all year around (but finite) - durable - stable - mostly liquid phase
5	Main operations	- biomass pre-treatment (e.g. drying, size reduction), - primary refining (e.g. pressing, hydrolysis, torrefaction, pyrolysis, hydro-thermal processing, digestion), - secondary refining (e.g. fermentation, gasification), - energy production (e.g. digestion/combustion and CHP production from process residues), - (catalytic) intermediate and final product upgrading (e.g. catalytic syngas conversion, catalytic synthesis from platform chemicals), - product separation. [Van Ree and Annevelink, 2007]	- crude oil preparation (e.g. blending), - primary distillation (e.g. atmospheric & vacuum distillation), - conversion (e.g. hydro-cracking, steam cracking, catalytic cracking, coking, visbreaking, including separation of undesirable compounds), - upgrading (i.e. 23 major and 16 minor unit processes, e.g. alkylation, catalytic reforming, hydrotreating, esterification, including separation of undesirable compounds). [Herrick et al., 1979; Kirk and Othmer, 1980; Ullmann, 1988; Wittcoff et al., 2004]
6	Process synthesis methods	These have not yet been established. Most likely, they will adapt the existing process synthesis methods; however, there should be some modifications regarding the characteristics of the feedstocks.	There are already established heuristic methods as well as simulation and control tools
7	Property databases	Limited and under development, e.g. - Phyllis (ECN) - Biomass Database (US-DoE)	Established databases, e.g. - CRC Handbook of Chemistry and Physics - Perry's Chemical Engineers' Handbook - Material Safety Data Sheets (MSDS) - Thermophysical property data for pure components and mixtures developed by The Design Institute for Physical Property Data (DIPPR)

(C) Process Integration - Both biomass and fossil feedstocks contain carbon and hydrogen that could be used for producing similar useful products. However, they have significant differences in their phases, densities, calorific values, and composition. According to ASTM D-4175, petroleum is defined as 'a naturally occurring mixture of hydrocarbons, generally in a liquid state, which may also

include compounds of sulphur, nitrogen, oxygen, metals, and other elements' [Speight, 2002]. Carbon and hydrogen contents of petroleum are 83-87% and 11-15%, whilst nitrogen, sulphur and oxygen contents are less than 15%, 6% and 3.5%, respectively [Nelson, 1958]. Biomass contains similar amounts of nitrogen and sulphur, but has up to 45% oxygen content. *Different characteristics of the feedstock lead to the use of different technologies, particularly in the upstream processing.*

The order of operations, material allocations, and the significance of separation processes or material purifications are other issues which need to be taken into account. The order of operations will affect the composition of subsequent output materials, which in biorefineries is usually irreversible. For this reason biomass components (excluding water) are classified into two chains according to their stability [Pertiwi, 2009]. Chain A is lignin > cellulose > hemicellulose > starches > sugars and chain B is proteins > oils/fats > vitamins (See Figure 3). An early analysis of various pre-treatments to lignocellulosic feedstocks suggested that for non-energy oriented biorefineries, the preferable order of separation and conversion processes would be (low temperature) physical treatments → (low temperature) physicochemical treatments → biological treatments → chemical treatments → product purification [Pertiwi, 2009].
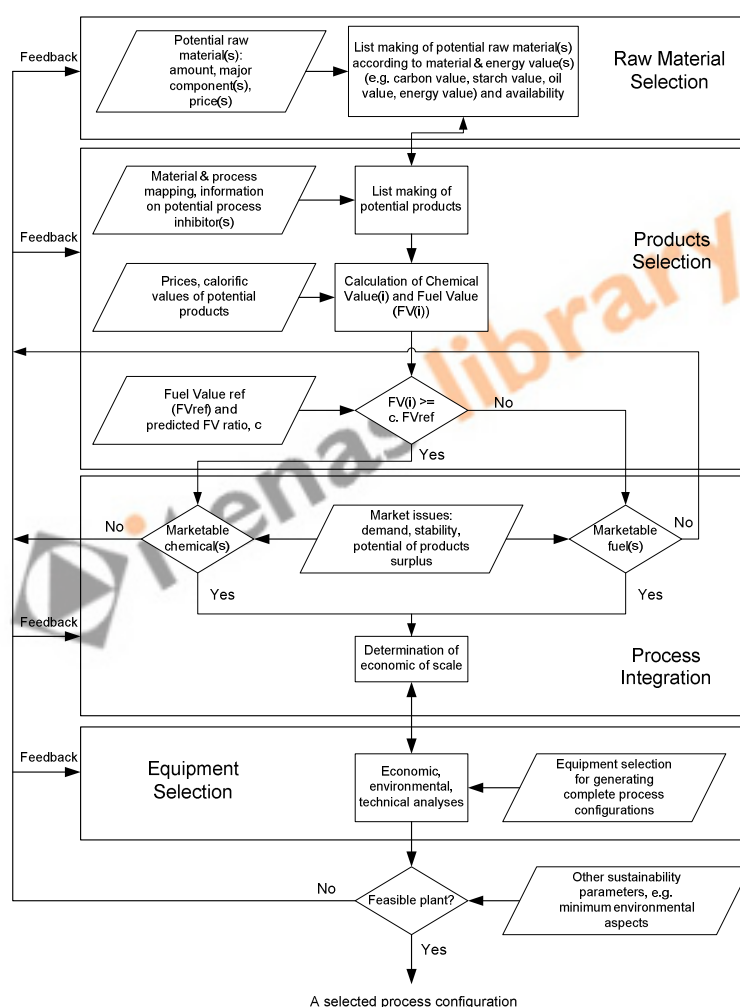

Figure 1: Biorefinery Synthesis Based on Proposed Heuristics and Suggested Parameters

Considering the different issues mentioned above, it can be concluded that in designing a new biorefinery for a particular raw material, the *first decision should be finding a technology producing the most valuable products from the least stable component*. Additional operations for by-products can then be added before or after this main operation, while material allocation should consider the potential impurities found in all the streams. For an existing biorefinery, if new and promising technologies are found, some retrofitting can also be implemented. In this case, the new by-products could potentially be more valuable than the existing products. To ensure the plant feasibility is

improved, *the additional investment and operating costs of the new technology should be relatively small compared to the new product sales*.

(D) Equipment Selection - Biorefineries deal with mainly solid phase materials (initially), whereas oil refineries process more fluids. However, the equipment selection method is excluded from this study, on the basis that *current heuristics in equipment selection and design are directly applicable*.
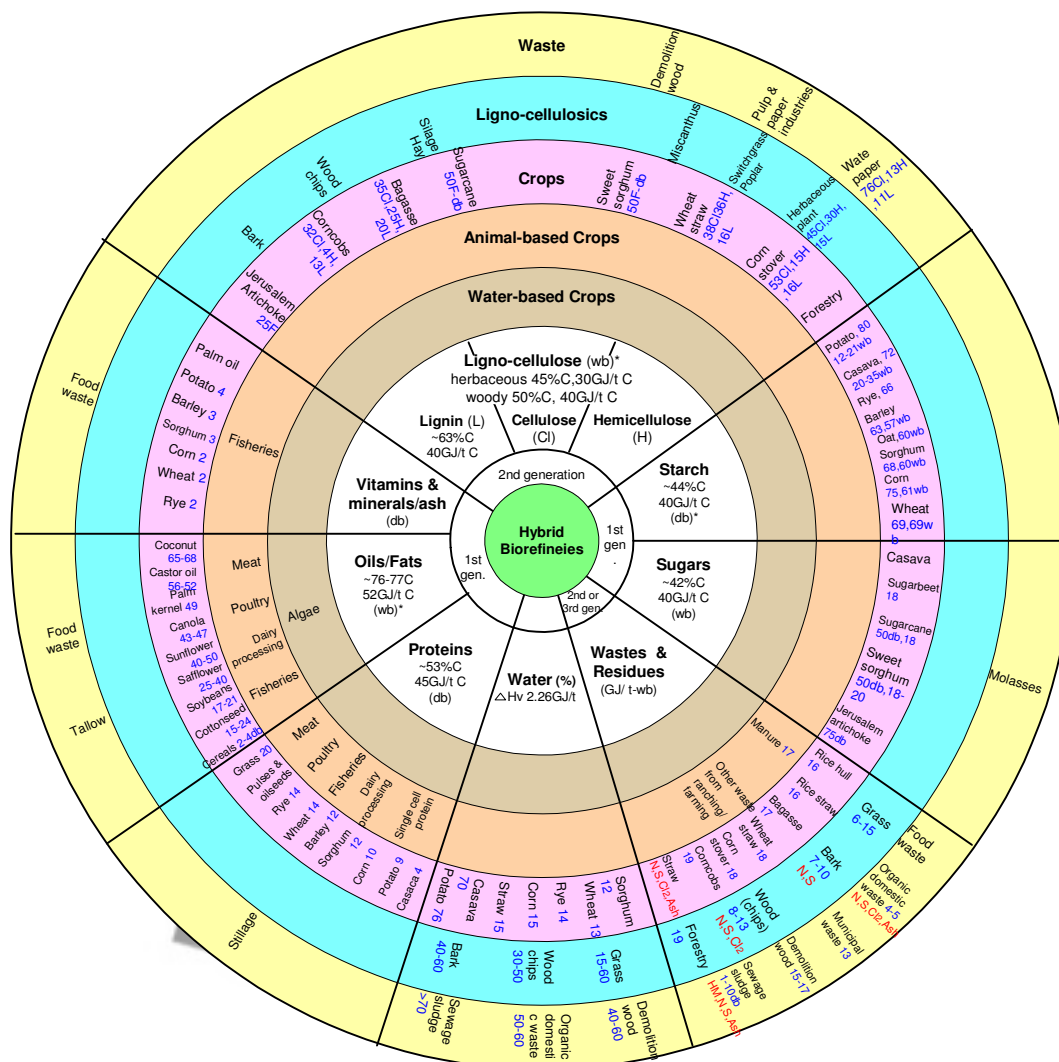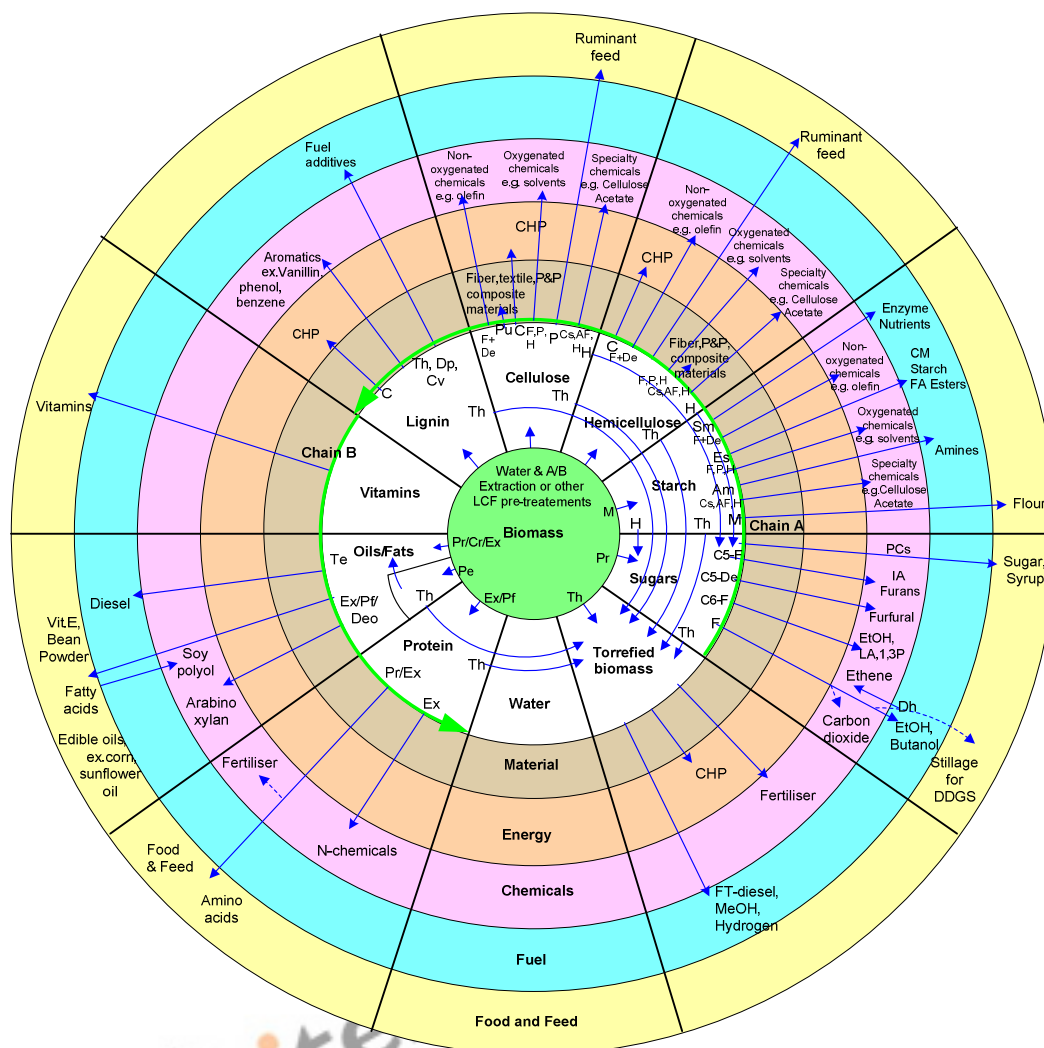

Note: C: carbon, Cl: cellulose, Cl_2: chlorine, db: dry basis, gen.: generation, GJ: gigajoule, HM: heavy metal, N: nitrogen, S: sulphur, wb: wet basis, ΔHv: heat of vaporisation, *: unless otherwise mentioned

Figure 2: Material Mapping for Biomass

3.2 Synthesis of Plausible Biorefineries Using the Evolutionary Optimisation Method

The concepts of biorefinery are still under development; however, potential gaps between process aspects of biorefineries and oil refineries have been found. The current Systematic Generation method is suggested not to be practical for biorefinery synthesis. On the other hand, Evolutionary Modification complemented by Superstructure Optimisation is expected to be more suitable. This approach is referred to as *Evolutionary Optimisation*. It consists of a superstructure generation modifying an existing process, followed by its optimisation. Predicted heuristics for the process modification can be generated and evaluated by following the PAR procedure. In the biorefinery context, the heuristics will be mainly aimed at the selection of raw material(s) and products and for process integration.

1,3 P	1,3-Propanediol	
AF	Aerobic fermentation	
Am	Amination	
C	Combustion	
C5	Five-carbon sugars	
C6	Six-carbon sugars	
CHP	Cogeneration Heat & Power	
CM	Carboxy-methyl	
Cr	Crushing	
Cs	Chemical synthesis	
De	Dehydration	
Deo	Deodorisation	
Dh	Dehydroxylation	
Dp	Depolymerisation	
EtOH	Ethanol	
Es	Esterification	
Ex	Extraction	
F	Anaerobic fermentation	
FA	Fatty acid	
FT	Fischer-Tropsch	
H	Hydrolysis	
IA	Itaconic acid	
LA	Lactic acid	
M	Milling	
P	Pyrolysis	
PCs	Platform chemicals	
Pe	Pearling	
Pf	Purification	
P&P	Pulp and paper	
Pr	Pressing	
Pu	Pulping	
Th	Thermochemical process	

Figure 3: Material & Process Mapping for Biorefineries

3.3 Modifications of the Corn Dry-Grind Process Using the Evolutionary Optimisation Method and the Evaluation Using Mass and Energy Values

A case study modifying the corn to ethanol dry-grind process is used to demonstrate the proposed tools and the Evolutionary Optimisation method. The components of corn used were 59.5% starch, 15% water, 8.33% protein, 7% hemicellulose/cellulose, 6.8% ash and 3.4% oil [Pertiwi, 2009]. The dry-grind process hydrolyses starch into sugars, which are then fermented into ethanol (as the main product, see Figure 3). It also produces Distiller's Dried Grain and Solubles (DDGS) as a by-product. Fibre (cellulose) and oil are envisioned to be intermediates of fine chemicals and DDGS price has been known to be dependent on protein content. The predicted heuristic was to *separate high value components (fibre and oil) before they are converted into lower value derivatives (DDGS)*. A superstructure was generated using the Elusieve process for back-end modification and the Quick

Germ (QG) and Quick Germ Quick Fibre processes for front-end modifications [Singh, 2006]. The Elusieve process is a fibre separation from DDGS using Sieving and Elutriation, while QG and QF are oil and fibre separations prior to ethanol fermentation, respectively. The QG is a pearling process shown in Figure 3. These processes are all designed to improve the quality of by-products (based on protein and fibre contents in DDGS) or for market diversification, and hence profitability. The GAMS 2.0.13.0 was used as the main simulation tool and was interfaced with Microsoft Excel spreadsheets.

The simulation results showed that front-end modifications were more feasible than back-end modification, which were indicated by the decreased Ethanol Production Costs (EPC) and Payback Periods [Pertiwi, 2009]. However, the Elusieve process can be used to improve the marketability of the by-products by providing a non-ruminant feed, i.e. DDGS whose cellulose content was less than 4wt-%. Moreover, the addition of the Elusieve process requires no further changes to the current process. Provided that modification is necessary and the markets are stable, the order of preferable modifications would be QG > QGQF > QG-Elusieve > Elusieve.

Corn competitiveness was compared to that of several other starch-rich biomass shown in the material mapping (See Figure 2). Table 2 shows that corn has relatively low Energy and Starch Values for the selected area (North America) and for the period of time considered (year 2004). The analysis was carried out based on the North America crops production because the US has been the biggest producer of corn-based bioethanol. There is also plenty of corn in stock, which is equivalent to 636 million tonnes of denatured ethanol/year.

Table 3 provides the calculation of Chemical and Fuel Values (FV) for ethanol, DDGS and the potential by-products. Diesel and gasoline prices are provided for comparison. The prices were set to be \$2/gal [EIA, 2009], which were the average prices in 2004. The heats of combustion for other chemicals were calculated according to their composition. The basis of these calculations was the Higher Heating Values (HHV) per carbon mass of carbohydrates, protein and lipids (See Figure 2). Lower Heating Values were estimated by adding all the HHVs of carbohydrates, protein and lipids in the products and subtracting the corresponding heat of vaporisation for water. The non-combustible nature of ash also reduced the heating value. The reduction caused by the ash per mass unit varies for different materials and depends on material moisture contents [Calle et al., 2007]. For all chemicals, it was estimated to be 10MJ/kg (See Table 4).

Table 2: Starch & Energy Values for Starch-rich Crops of North America in 2004[1]

Feedstock	Stock (10⁶t/a)	Exports (10⁶t/a)	Farm Price (\$(2004)/t)	Energy Content (GJ/t)	Energy Value (\$(2004)/GJ)	Starch Content wb-%	Starch Value (\$(2004)/t)
Corn	1942	1950	76.37	17.45	4.38	61.13	1.25
Wheat	579	1000	132.28	17.40	7.60	69.44	1.90
Barley	122	16	97.63	16.00	6.10	57.31	1.70
Oat*	58	3	55.12	17.27	3.19	59.66	0.92
Sorghum	57	176	69.29	15.75	4.40	60.50	1.14

[1]Pertiwi [2009]. *The starch content is the nitrogen-free extract.

Table 3: Chemical & Fuel Values of Potential Products/By-Products for the Modified Dry–Grind Process

Organic Chemicals	LHV[4] (MJ/kg)	Chemical Value(\$/kg)	Fuel Value[3] (\$/MJ)
DDGS – base case	27.26[1]	0.098	3.60E-03
DDGS – ruminants	36.94[1]	0.144	3.90E-03
DDGS – non ruminants	9.34[1]	0.036	3.85E-03
Corn fibre	33.98[1]	0.042	1.24E-03
Germ[5]	41.63[1]	0.287	6.89E-03
References			
- Ethanol	26.80[2]	5.550	2.07E-01
- Conventional diesel	37.40[2]	5.750	1.54E-01
- Gasoline	44.00[2]	6.270	1.43E-01

[1]Table 4. [2]Kosaric et al. [2001]. [3]Fuel Value = Chemical Value/LHV. [4]Lower Heating Value. [5]Product of the QG process.

The FV of by-products from both modifications were compared to the FV of the base case DDGS because the modifications would only affect the type and characteristic of the former DDGS, but not the FV of ethanol. This quantitative analysis was in accordance with the simulation results. The FV of the germ from the QG process, which was the most preferable modifying process, was almost doubled. The FVs of the Elusieve by-products (fibre, DDGS for ruminants and DDGS for non-ruminants), on the contrary, were similar to or lesser than those of the base case DDGS. Corn fibre was also the product of the QF process, which was applied to the product of the QG process. The simulation results showed that the addition of the QF after the QG unit increased the PP and the EPC. The QF process, therefore, was not added to the material & process mapping. The QGQF, however, was still more favourable than the addition of the Elusieve process due to the high FV of the germ from the QG process. Further investigations of FVs for different bioprocesses are required to derive a specific FV ratio that would be reliable as a reference for general biorefinery modification.

Table 4: Estimated Heat of Combustion of Potential By-products for the Modified Dry-Grind Process

Organic Chemicals	Composition in product[1] (kt/a)					Estimated LHV (MJ/kg)
	Carbohydrates (39.8 MJ/kg)	Protein (45.3 MJ/kg)	Oils/fats (52 MJ/kg)	Ash (10MJ/kg)	Water (ΔHv 2.26MJ/kg)	
DDGS – base case	54.915	38.158	15.224	35.785	14.25	27.26
DDGS – ruminants	37.443	30.049	10.551	4.229	8.137	36.94
DDGS – non ruminants	8.338	6.524	3.738	30.584	4.865	9.34
Corn fibre	9.134	1.585	0.934	0.972	1.248	33.98
Germ[2]	8.759	5.639	9.622	0	2.378	41.63

[1]Pertiwi [2009]. [2]Product of the QG process. Ash and water heating values were subtracted from the HHVs of dry materials [Calle et al., 2007].

4. Conclusion

Biorefinery synthesis is envisaged to have special heuristics addressing the unique characteristics of biomass, such as the proposed heuristic specifying the "*separation of high value components before they are converted into lower value derivatives*". The development of these heuristics will require some reasonable amount of modelling & simulations, which can potentially be supported by the proposed Evolutionary Optimisation and the existing PAR procedure. The proposed metrics need to be evaluated, in particular to calculate the expected Fuel Value ratio. Material and material & process mappings also need to be updated continuously for the development of raw material, product and (integrated) process databases. The availability and practical applications of these relevant heuristics and the corresponding tools are expected to foster new and exciting innovations in biorefineries.

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